

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 November 2001 (08.11.2001)

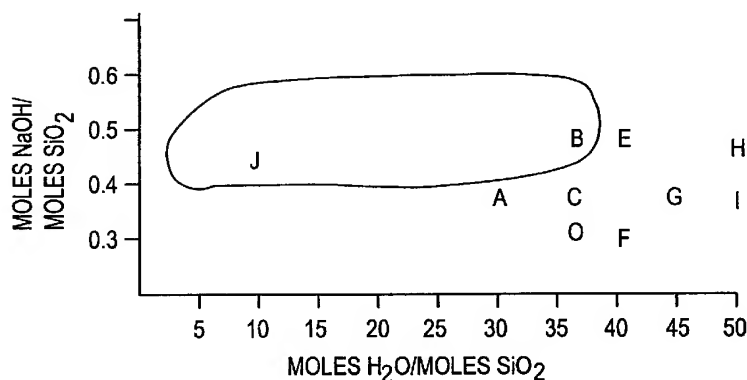
PCT

(10) International Publication Number
WO 01/83370 A2

- (51) International Patent Classification⁷: **C01B 33/38**
- (21) International Application Number: PCT/US01/11978
- (22) International Filing Date: 12 April 2001 (12.04.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/197,250 14 April 2000 (14.04.2000) US
- (71) Applicant (for all designated States except US): **THE DOW CHEMICAL COMPANY** [US/US]; 2030 Dow Center, Midland, MI 48674 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **GARCES, Juan, M.** [US/US]; 1106 West Sugnet Road, Midland, MI 48640 (US). **LAKSO, Steve, R.** [US/US]; 3634 West Chippewa River Road, Shepherd, MI 48883 (US). **SCHOEMAN, Brian, J.** [SE/US]; 410 Lingle Lane, Midland, MI 48642 (US).
- (74) Agent: **ULMER, Duane, C.**; The Dow Chemical Company, 2301 N. Brazosport Boulevard, Building B-1211, Freeport, TX 77541-3257 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: SYNTHETIC PLATY MAGADIITE AND OCTASILICATE



(57) Abstract: A method for producing synthetic magadiite, including the step of: heating a liquid aqueous colloidal silica suspension, the liquid aqueous colloidal silica suspension having a mole ratio of sodium hydroxide to silica and a mole ratio of water to silica effective to produce a synthetic magadiite wherein more than fifty percent by weight of the synthetic magadiite is platy synthetic magadiite. The synthetic platy magadiite can be converted to the acid form and: (a) heated to produce quartz-like plates; or (b) alkylated to produce an organophilic material. In another aspect, the instant invention is a method for the production of platy sodium octasilicate which includes the step of: heating a liquid aqueous colloidal silica dispersion containing silica, sodium oxide, and water, the mole ratio of the silica to the sodium oxide being in the range of from about 3.5 to about 10. In another aspect, the instant invention is a method for preparing a liquid aqueous colloidal silica dispersion, the dispersion having a mole ratio of silica to sodium oxide of from 3.5 to 10, which includes the step of: mixing a sufficient amount of liquid aqueous colloidal silica suspension with a liquid aqueous sodium silicate suspension to produce the liquid aqueous colloidal silica dispersion, the liquid aqueous colloidal silica suspension having a mole ratio of silica to sodium oxide of more than 20, the liquid aqueous sodium silicate suspension having a mole ratio of silica to sodium oxide of less than 3.5, the rate of mixing being effective to prevent the gellation or solidification of the liquid aqueous colloidal silica dispersion.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SYNTHETIC PLATY MAGADIITE AND OCTASILICATE

GOVERNMENT CONTACT

5 This application is under a Government contract with
The Department of Commerce (NIST) - Advanced Technology
Program Project #70NANB7H3028.

10 The instant invention is in the field of layered
hydrated crystalline polysilicates. More specifically,
the instant invention relates to magadiite and
octasilicate layered hydrated crystalline polysilicates.

15 Makatite ($\text{Na}_2\text{O} \cdot 4\text{SiO}_2 \cdot 5\text{H}_2\text{O}$), kanemite ($\text{Na}_2\text{O} \cdot 4\text{SiO}_2 \cdot 7\text{H}_2\text{O}$),
octasilicate ($\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$), magadiite ($\text{Na}_2\text{O} \cdot 14\text{SiO}_2 \cdot 10\text{H}_2\text{O}$)
and kenyaite ($\text{Na}_2\text{O} \cdot 22\text{SiO}_2 \cdot 10\text{H}_2\text{O}$) are a series of sodium
polysilicate hydrates, Almond et al., "A structural
consideration of kanemite, octasilicate, magadiite and
kenyaite". Makatite, kanemite, octasilicate, magadiite
20 and kenyaite are useful, for example, in the preparation
of materials for catalysis.

25 Magadiite was first discovered as a natural material
and then synthesized in the laboratory. Natural magadiite
tends to be in the form of several nanometer thick square
plates that are several micrometers on a side. However,
synthetic magadiite tends to be in the form of spherical
cabbage-like aggregates about ten micrometers in diameter,
Garces, et. al., Clays and Clay Minerals, 1988, 409-418.
30 Synthetic magadiite can prepared hydrothermally by heating
a colloidal silica suspension characterized as 9 moles of
 SiO_2 , 2 moles of NaOH and 75 moles of water at 100 degrees
Celsius for 4 weeks, Lagaly et al., Am. Mineral. 1975,
642.

The "aspect ratio" (plate length/plate thickness) of magadiite in the form of individual plates is relatively high (100 or more). The aspect ratio of magadiite in the form of cabbage-like aggregates is relatively low (about 1).

Fillers dispersed in a polymer are well known to improve some of the physical properties of the polymer such as the tensile and flex modulus of the polymer. When at least one dimension of the filler is less than one micron and when the aspect ratio of the filler is relatively high, then the improvement can be especially beneficial, that is, "nanocomposite polymer systems", for example, United States Patent 5,717,000. Therefore, natural magadiite would be expected to be useful to prepare a nanocomposite polymer system. However, natural magadiite is relatively expensive for such an application. Synthetic magadiite is expected to be less expensive but its low aspect ratio would not allow its use to make a nanocomposite polymer. It would be an advance in the art if a synthetic magadiite could be prepared in the form of separate plates rather than as cabbage-like agglomerates.

Octasilicate tends to be in the form of several nanometer thick plates, which are several microns on a side. Therefore, octasilicate is an excellent candidate to be used as a filler in a nanocomposite polymer system. However, octasilicate is synthesized by a solid state reaction taking 3-4 weeks, McCulloch, J. Am. Chem. Soc., 1952, 2453. It would be an advance in the art if a faster liquid phase method for preparing octasilicate could be developed.

The instant invention, in one embodiment, is a method for producing synthetic magadiite, comprising the step of: heating a liquid aqueous colloidal silica suspension, the liquid aqueous colloidal silica suspension having a mole
5 ratio of sodium hydroxide to silica and a mole ratio of water to silica effective to produce a synthetic magadiite wherein more than fifty percent by weight of the synthetic magadiite is platy synthetic magadiite.

10 In another embodiment, the instant invention is synthetic magadiite wherein more than fifty percent by weight of the synthetic magadiite is in the form of individual plates.

15 In another embodiment, the instant invention is a silica gel made by contacting the synthetic platy magadiite with an acid in an aqueous liquid.

In another embodiment, the instant invention is
20 synthetic platy magadiite wherein at least a portion of the sodium ions of the synthetic platy magadiite are exchanged for hydrogen ions to produce acidified synthetic platy magadiite.

25 In another embodiment, the instant invention is the acidified synthetic platy magadiite sufficiently heated to drive off water from the acidified synthetic platy magadiite to form silica plates.

30 In another embodiment, the instant invention is the acidified synthetic platy magadiite wherein the surface hydroxyls of the acidified synthetic platy magadiite are alkylated.

In another embodiment, the instant invention is a method for the production of platy sodium octasilicate, comprising the step of: heating a liquid aqueous colloidal silica dispersion containing silica, sodium
5 oxide, and water, the mole ratio of the silica to the sodium oxide being in the range of from about 3.5 to about 10.

In another embodiment, the instant invention is a
10 method for preparing a liquid aqueous colloidal silica dispersion, the dispersion having a mole ratio of silica to sodium oxide of from 3.5 to 10, comprising the step of: mixing a sufficient amount of liquid aqueous colloidal
15 silica suspension with a liquid aqueous sodium silicate suspension to produce the liquid aqueous colloidal silica dispersion, the liquid aqueous colloidal silica suspension having a mole ratio of silica to sodium oxide of more than 20, the liquid aqueous sodium silicate suspension having a
20 mole ratio of silica to sodium oxide of less than 3.5, the rate of mixing being effective to prevent the gellation or solidification of the liquid aqueous colloidal silica dispersion.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Fig. 1 is a plot of moles of NaOH/SiO₂ v. Moles of H₂O/SiO₂ showing various results within and outside of the instant invention;

Fig. 2 is a photomicrograph of platy synthetic magadiite of the instant invention;

30 Fig. 3 is is a photomicrograph of synthetic magadiite of the prior art showing the cabbage-like agglomerates associated therewith;

Fig. 4 is graph showing mole ratio of SiO₂ to Na₂O for various aqueous colloidal silica systems;

Fig. 5 is a photomicrograph of platy synthetic octasilicate made by the method of the instant invention.

DETAILED DESCRIPTION OF THE INVENTION

5 Referring now to Fig. 1, therein is shown a plot of moles of NaOH/SiO_2 v. moles of $\text{H}_2\text{O}/\text{SiO}_2$ showing various results A-F within and outside of the instant invention. Each colloidal silica suspension described in Fig. 1 is heated to 160 degrees Celsius for 24 hours to produce
10 synthetic magadiite, which is then examined by electron microscopy. The result for A is more single plates than cabbage-like agglomerates on a weight basis. The result for B is essentially all single plates shown in Fig. 2. The result for C is essentially all cabbage-like
15 agglomerates shown in Fig. 3. The result for D is mostly amorphous silica. The result for E is mostly cabbage-like agglomerates with some plates on a weight basis. The result for F is mostly cabbage-like agglomerates. The result for G is cabbage-like agglomerates. The result for
20 H is cabbage-like agglomerates. The result for I is mostly cabbage-like agglomerates with a some plates on a weight basis. The result for J is essentially all plates. The oval drawn on Fig. 1 shows the preferred range of the mole ratio of sodium hydroxide to silica and water to
25 silica of the instant invention. The most preferred range of the mole ratio of sodium hydroxide to silica and water to silica of the instant invention would be a smaller oval inside the oval shown in Fig. 1. In the broad scope of the instant invention, the mole ratio of sodium hydroxide
30 to silica and a mole ratio of water to silica must be effective to produce a synthetic magadiite wherein more than fifty percent by weight of the synthetic magadiite is platy synthetic magadiite.

The temperature used is preferably from about 140 degrees to about 170 degrees. At temperatures above 170 degrees, for example, 180 degrees or 190 degrees or 200 degrees Celsius, the yield of platy synthetic magadiite is progressively lower. At temperatures below 140 degrees Celsius, for example, 130 degrees, 120 degrees or 110 degrees Celsius, the rate of formation of platy synthetic magadiite is progressively slower. However, adding magadiite seed, for example, at the 10 weight percent level, to the aqueous collodial silica suspension reduces the time needed at 160 degrees Celsius to 8 hours or less.

The synthetic magadiite produced is more than fifty percent by weight in the form of individual plates v. the cabbage-like agglomerates. More preferably, the synthetic magadiite produced is more than eighty percent by weight in the form of individual plates v. the cabbage-like agglomerates. Most preferably, the synthetic magadiite produced is more than ninety percent by weight in the form of individual plates v. the cabbage-like agglomerates and contains less than two percent by weight of amorphous silica.

When the platy magadiite of the instant invention is contacted with an acid in an aqueous suspension, then a new form of silica gel is produced (having a network of plates). Similarly, when the platy magadiite of the instant invention is contacted with colloidal silica and an acid in an aqueous suspension, then another new form of silica gel is produced (having a network of plates and spheres).

At least a portion of the sodium ions of the synthetic platy magadiite of the instant invention can be

exchanged for hydrogen ions to produce acidified synthetic platy magadiite. When the portion of the sodium ions of the synthetic platy magadiite of the instant invention is ninety percent or more and such acidified synthetic platy magadiite (or perhaps more accurately platy silica) is heated sufficiently to drive off water, then the acidified synthetic platy magadiite is converted into quartz-like silica plates. On the other hand, the acidified synthetic platy magadiite can also be alkylated via the Si-O-H moiety to produce Si-O-R, where the R group is an alkyl group, for example, butyl. Such alkylated materials are lipophylic and as such are more compatible with many polymers. A fraction of B₂O₄ can be substituted for the SiO₂ so that the boron-substituted platy synthetic magadiite can be treated with sodium aluminate to produce an aluminated platy synthetic magadiite to be used, for example, as a catalyst activator.

Referring now to Fig. 4, therein is a graph showing mole ratio of SiO₂ to Na₂O for various aqueous colloidal silica systems. Such systems tend to be stable and liquid in the "A" regions. However, such systems tend to be unstable and not liquid in the "B" region. In the "B" region, the system tends to gel and form a solid.

The instant invention, in one of its embodiments, is a solution to this problem. Using the instant invention a liquid aqueous colloidal silica dispersion having a mole ratio of silica to sodium oxide of from 3.5 to 10 can be prepared by first preferably cooling a liquid aqueous sodium silicate suspension to less than ten degrees Celsius, the liquid aqueous sodium silicate suspension having a mole ratio of silica to sodium oxide of less than 3.5 and then mixing a sufficient amount of liquid aqueous

colloidal silica suspension to the cooled liquid aqueous sodium silicate suspension to produce the liquid aqueous colloidal silica dispersion, the liquid aqueous colloidal silica suspension having a mole ratio of silica to sodium oxide of more than 20, the rate of mixing being effective to prevent the gellation or solidification of the liquid aqueous sodium silicate suspension. It should be understood that although not preferred, substituting an acid for the liquid aqueous colloidal silica suspension in the above procedure is equivalent in the instant invention. Similarly, it should be understood that although not preferred, substituting a base for the liquid aqueous sodium silicate suspension is equivalent in the instant invention.

15

For example, 78.45 grams of sodium silicate (PQ Corp., PQ-N, 28.2 wt% SiO₂, 8.7 wt% Na₂O) is cooled to a temperature below 5°C in a sonicator bath containing ice and water with stirring and no sonication. The sonicator is then started and 21.7g colloidal silica (Ludox HS-40, duPont, approx. 40 wt% SiO₂, trace amounts of Na₂O) is gradually added drop-wise to the heel of sodium silicate while continually stirring in a vigorous manner. The rate of addition is such that little visible solid amorphous precipitate is formed. During the course of addition, the bath is kept cool by the ice. Then the resulting liquid aqueous colloidal silica dispersion having a mole ratio of silica to sodium oxide of about 4.6 is heated at 105 degrees Celsius for 10 days to produce the octasilicate shown in Fig. 5. Adding octasilicate seed to the liquid aqueous colloidal silica dispersion at the 0.8 weight percent level reduces the time needed to 3 days (and one day if the liquid aqueous colloidal silica dispersion is agitated).

30

The temperature used to heat the liquid aqueous colloidal silica dispersion preferably is in the range of from 50 to 170 degrees Celsius. At temperatures progressively lower than about 100-110 degrees Celsius, the time needed is increased. At progressively higher temperatures, such as 125 degrees Celsius or 155 degrees Celsius, the octasilicate tends to redissolve and form magadiite and kenyaite at a progressively higher rate.

10 The mole ratio of the silica to the sodium oxide in the liquid aqueous colloidal silica dispersion is preferably in the range of from 4 to about 10, more preferably in the range of from about 4 to about 6, yet more preferably in the range of from about 4.3 to about 5.2 and most preferably in the range of from about 4.5 to about 4.7. A fraction of B_2O_4 can be substituted for the SiO_2 in the liquid aqueous colloidal silica dispersion so that the boron-substituted octasilicate can be treated with sodium aluminate to produce an aluminated
15 octasilicate and used, for example, as a catalyst
20 activator.

WHAT IS CLAIMED IS:

1. A method for producing synthetic magadiite, comprising the step of: heating a liquid aqueous colloidal silica suspension, the liquid aqueous colloidal silica suspension having a mole ratio of sodium hydroxide to silica and a mole ratio of water to silica effective to produce a synthetic magadiite wherein more than fifty percent by weight of the synthetic magadiite is platy synthetic magadiite.
2. The method of Claim 1, wherein the mole ratio of sodium hydroxide to silica is in the range of from about 0.4 to about 0.5, the mole ratio of water to silica is in the range of from about 5 to about 39.
3. The method of Claim 1, wherein the mole ratio of sodium hydroxide to silica is in the range of from about 0.48 to about 0.52, the mole ratio of water to silica is in the range of from about 25 to about 39.
4. Synthetic magadiite wherein more than fifty percent by weight of the synthetic magadiite is platy magadiite.
5. Synthetic magadiite wherein more than eighty percent by weight of the synthetic magadiite is platy magadiite.
6. Synthetic magadiite wherein more than ninety percent by weight of the synthetic magadiite is platy magadiite.

7. Silica gel made by contacting the synthetic platy magadiite of Claims 4, 5 or 6 with an acid in an aqueous liquid.
- 5 8. Silica gel made by contacting the synthetic platy magadiite of Claims 4, 5 or 6 with colloidal silica and an acid in an aqueous liquid.
- 10 9. The synthetic platy magadiite of Claims 4, 5 or 6 wherein at least a portion of the sodium ions of the synthetic platy magadiite are exchanged for hydrogen ions to produce acidified synthetic platy magadiite.
- 15 10. The synthetic platy magadiite of Claim 9, wherein more than ninety percent of the sodium ions of the synthetic platy magadiite are exchanged for hydrogen ions to produce acidified synthetic platy magadiite.
- 20 11. The acidified synthetic platy magadiite of Claim 10, sufficiently heated to drive off water from the acidified synthetic platy magadiite to form silica plates.
- 25 12. The acidified synthetic platy magadiite of Claims 9 or 10, wherein the surface hydroxyls of the acidified synthetic platy magadiite are alkylated.
- 30 13. The synthetic platy magadiite of Claim 12, wherein the surface hydroxyls of the acidified synthetic platy magadiite are butylated.

14. A method for the production of platy sodium octasilicate, comprising the step of:
heating a liquid aqueous colloidal silica dispersion containing silica, sodium oxide,
and water, the mole ratio of the silica to the sodium oxide being in the range of from about 3.5 to about 10.
15. The method of Claim 14, wherein the temperature is in the range of from about 80 to about 125 degrees Celsius and the mole ratio of the silica to the sodium oxide is in the range of from about 4 to about 6.
16. The method of Claim 14, wherein the temperature is in the range of from about 95 to about 115 degrees Celsius and the mole ratio of the silica to the sodium oxide is in the range of from about 4.3 to about 5.2.
17. The method of Claim 14, wherein the temperature is in the range of from about 100 to about 110 degrees Celsius and the mole ratio of the silica to the sodium oxide is in the range of from about 4.5 to about 4.7.
18. A method for preparing a liquid aqueous colloidal silica dispersion, the dispersion having a mole ratio of silica to sodium oxide of from 3.5 to 10, comprising the step of: mixing a sufficient amount of liquid aqueous colloidal silica suspension with a liquid aqueous sodium silicate suspension to produce the liquid aqueous

colloidal silica dispersion, the liquid aqueous colloidal silica suspension having a mole ratio of silica to sodium oxide of more than 20, the liquid aqueous sodium silicate suspension having a mole ratio of silica to sodium oxide of less than 3.5, the rate of mixing being effective to prevent the gellation or solidification of the liquid aqueous colloidal silica dispersion.

19. The method of Claim 18, wherein the liquid aqueous colloidal silica dispersion has a mole ratio of silica to sodium oxide of from 4 to 10.

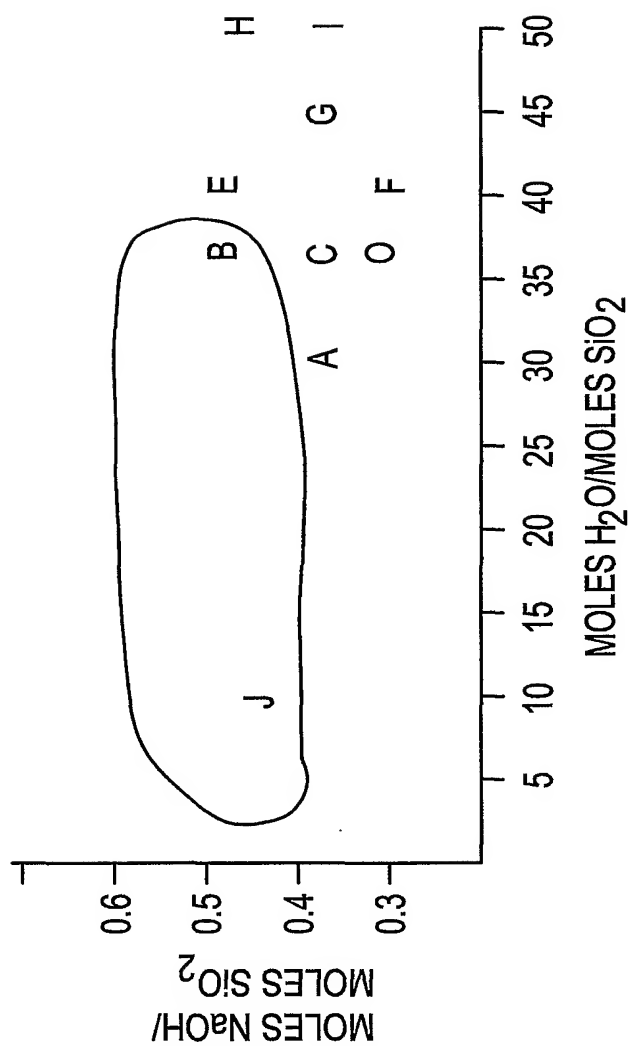
20. The method of Claim 18, wherein the liquid aqueous colloidal silica dispersion has a mole ratio of silica to sodium oxide of from 4 to 6.

21. The method of Claim 18, wherein the liquid aqueous colloidal silica dispersion has a mole ratio of silica to sodium oxide of from 4.5 to 5.2.

22. The method of Claim 18, wherein the liquid aqueous colloidal silica dispersion has a mole ratio of silica to sodium oxide of from 4.5 to 4.7.

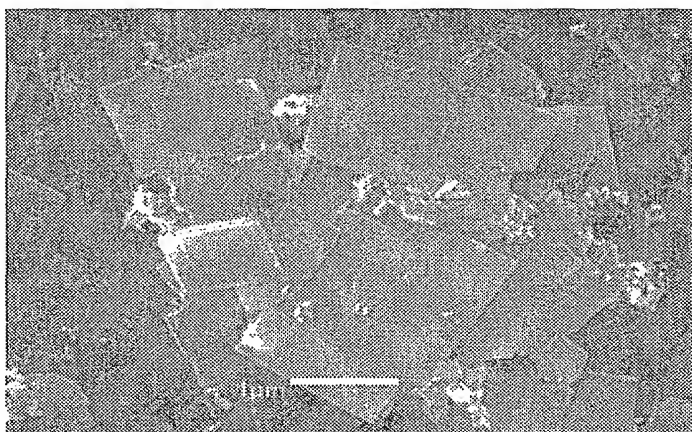
1/5

FIG. 1



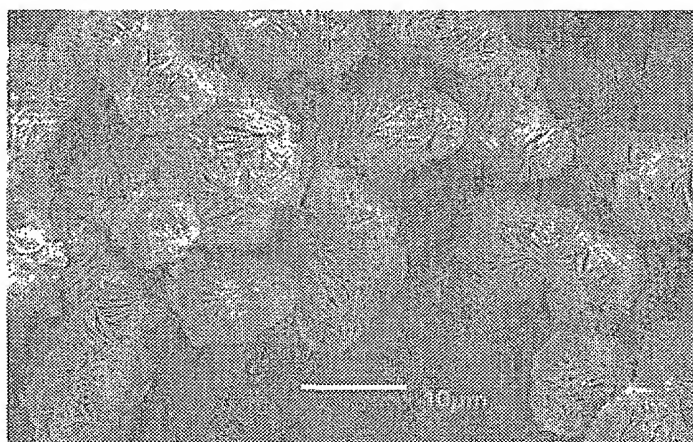
2/5

FIG. 2



3/5

FIG. 3
PRIOR ART



4/5

FIG. 4

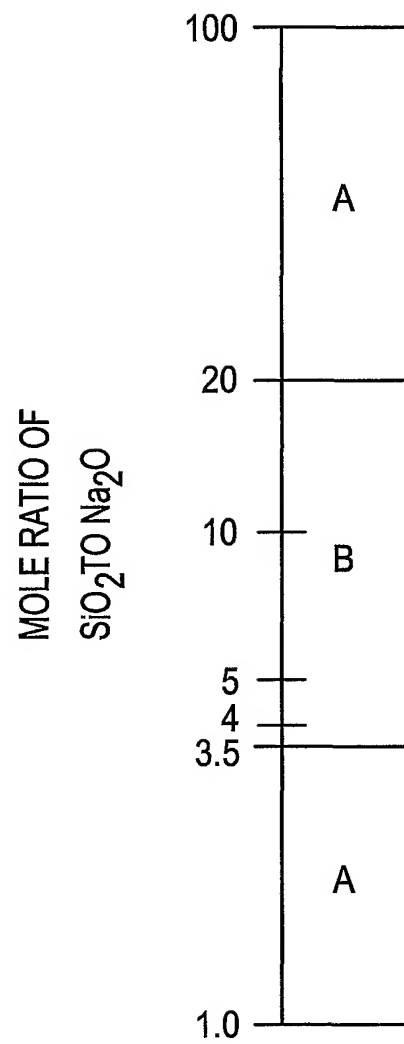


FIG. 5

